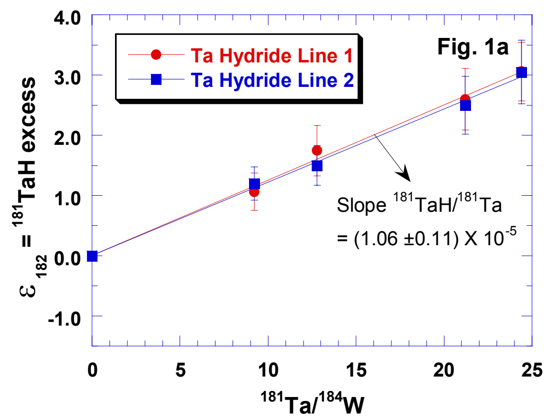
CAUTIONARY NOTES ON COSMOGENIC ^{182}W AND OTHER NUCLEI IN LUNAR SAMPLES. Qingzhu Yin[1] , Stein B. Jacobsen[1] and G. J. Wasserburg [1,2] [1]Department of Earth and Planetary Sciences, Harvard University, 20 Oxford Street, Cambridge, MA 02138, USA. yin@fas.harvard.edu [2]The Lunatic Asylum, Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, USA.

Introduction: Leya et al. (2000) [1] showed that neutron capture on ^{181}Ta results in a production rate of ^{182}Ta (decays with a half-life of 114 days to ^{182}W) sufficiently high to cause significant shifts in ^{182}W abundances considering the neutron fluences due to the cosmic ray cascade that were known to occur near the lunar surface (Lingenfelter et al., 1972; Russ et al. 1972; Curtis and Wasserburg, 1975; Woolum et al., 1975; Nishiizumi et al., 1997) [2, 3, 4, 5, 6]. Leya et al. [1] concluded that this cosmogenic production of ^{182}W may explain the large positive ε_{182W} values that Lee et al. (1997) [7] had reported in some lunar samples rather than being produced from decay of now extinct ^{182}Hf ($\bar{\tau} = 13 \times 10^6$ yr). If the large range in ε_{182W} of lunar samples (0 to +11 in whole rock samples) was due to decay of now extinct ^{182}Hf, it would require a very early time of formation and differentiation of the lunar crust-mantle system (with high Hf/W ratios) during the earliest stages of Earth's accretion. This result was both surprising and difficult to understand. The ability to explain these results by a more plausible mechanism is therefore very attractive. In a recent report Lee et al. (2002) [8] showed that there were excesses of ^{182}W and that ε_{182W} was correlated with the Ta/W ratios in the mineral phases of individual lunar rock samples. This is in accord with ^{182}W variations in lunar samples being produced by cosmic-ray induced neutron capture on ^{181}Ta.

Results and Discussions: While our considerations of ^{182}W production due to neutron capture on ^{181}Ta are in general agreement with the results presented by Leya et al. [1] and Lee et al. [8], there are some additional points that merit attention. The first of these is analytical, the second is isotope systematics, and the third is the relationship between irradiation ages and neutron fluence for different systems.

From an analytical consideration there is always the issue of eliminating isobaric interferences. One possible source of apparent ^{182}W excess is the presence of ^{181}TaH. To test this, several solutions of normal Ta and W were prepared with different proportions and analyzed with the MC-ICP-MS (Micromass IsoProbe®) in the EPS Department at Harvard. The results are shown in Figure 1. It was found that there was a very precise linear correlation between the apparent ε_{182W} ("ε_{182}") and the ^{181}Ta/^{184}W in the solution, where $\varepsilon_{182} = [(^{182}\mathrm{I}/^{183}\mathrm{W}) / (^{182}\mathrm{W}/^{183}\mathrm{W}) - 1] \times 10^4$, and $^{182}\mathrm{I} = {}^{182}\mathrm{W} + {}^{181}\mathrm{TaH}$.



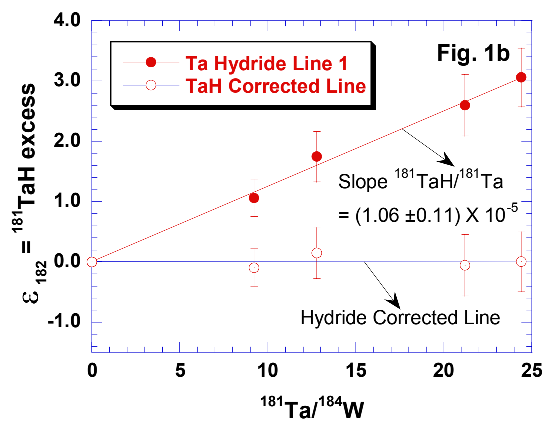


Fig. 1a. Tantalum hydride production by MC-ICP-MS. Four Ta-W mixture solutions were prepared. Ta concentration was kept at ~300 ppb, while the W concentrations were 41, 47, 78 and 108 ppb, respectively. The point at the origin is a pure W standard solution without Ta. The solutions were measured twice, once ^{181}Ta simultaneously measured (red) with other W isotopes, another without monitoring ^{181}Ta (blue). The excesses on mass 182 correlate positively with Ta/W ratios. The slope corresponds to the precisely determined Ta hydride production level at ^{181}TaH/^{181}Ta = (1.06 ±0.11)x10^{-5} in the MC-ICP-MS used for the experiment. All measured W isotopes (^{182}W-^{183}W-^{184}W-^{186}W) except ^{182}W were normal in these experiments.

Fig. 1b. Illustrates that if the ^{181}Ta peak is monitored in parallel experiments with lunar samples with high Ta/W ratios, instrumental artifact due to ^{181}TaH production overlapping with ^{182}W could be precisely corrected.

The slope obtained from Figure 1 is ^{181}TaH/^{181}Ta = 1.1×10^{-5}. This agrees with a direct measurement of ^{181}TaH/^{181}Ta = 1.2×10^{-5} for a pure Ta solution. This

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value was found in two experiments. In Figure 1a, ("ε_{182}") = 1 corresponds to ^{181}Ta/^{184}W = 10 (equivalent to Ta/W = 3). The slope is roughly within the range found for the three "cosmochrons" in Lee et al. [8]. It is evident that unless effective separation of Ta from the W solutions is done prior to analysis, there is a risk of hydride interferences causing an erroneous measurement of the ^{182}W/^{183}W ratio. We do not wish to imply that the existing lunar data are in error but simply emphasize the need for care in the chemical separation and mass spectrometry.

The second issue is that for well-behaved mineral systems within a single small rock sample it is expected that the data should lie on a straight line within errors, and that the initial values should be reasonable. For the data so far available, there is considerable scatter in all of the Ta-W cosmochron correlation lines as well as a wide range in initial values for the different rock samples (from ε_{182W} = 1.0 to 4.7 with large uncertainties ±2.3 to ±3.6, Figure 1 of Lee et al. [8]). In general no ε_{183W} is reported so that identifying other irregularities is not possible.

Finally there is the broader question of the intercomparison of irradiation history for different nuclides in the same sample. For example, the mare basalt 15555 shows a zero slope line of ε_{182W} versus ^{181}Ta/^{184}W (Figure 2 of Lee et al. [8]) and an initial ε_{182W} = 1.30±0.39, indicating a very low exposure age. The young "exposure age" is 90±10 Ma for #15555 as determined by the cosmogenic ^{38}Ar (Podosek et al.) [9]. This would appear to be consistent with the absence of a correlated ^{182}W effect. However, it must by noted that Nyquist et al. (Table 2) [10] reported neutron capture effects on Sm of ε_{149Sm} = -5.0±0.4 for #15555 which has no ^{182}W excess and ε_{149Sm}=-4.3±0.4 for #75075 (as found also by Lugmair et al.) [11] which has a large ^{182}W excess and implies substantial neutron fluences. There is thus no direct relationship between the neutron fluences by the different methods on these two samples. Further, for #15555, the low ^{38}Ar cosmogenic age and the considerable neutron exposure of Sm and the negligible neutron exposure found from ^{182}W must be reconciled. If the error estimates of ε_{182W} are increased, it is possible that for the low Ta/W ratios of #15555 resolution of a slope significantly different from zero in the ε_{182} vs. Ta/W plot may have been below that detection limits. Irradiation of material buried at substantial depths for long times (~3×10^9 y) which are then excavated within the last 10^8 years will yield very different results for different nuclides. In order to explain the absence of ^{182}W effects for #15555, it may be necessary to appeal to differences in the energy spectrum during the irradiation and exposures at shallow and deep depth. Since the resonances of ^{181}Ta start at ~ 4 eV, the ^{181}Ta behavior is different from that of either ^{155}Gd or ^{149}Sm. It is not at all evident that any of the above effects could explain the disparate results. It follows that direct comparison of irradiation histories and of the fluences as calculated for different systems may not, by a large margin, be possible.

Conclusions: We conclude that until there is a clear understanding of these issues, any interpretation of ε_{182W} values for lunar samples should be treated with caution. With regard to the general discrepancies between cosmic ray exposure ages, there still remain several important, unresolved issues. In future investigations, it will be valuable to measure and document cosmogenic effects on W, Sm, Gd, spallation products etc. from the same split of a sample.

Acknowledgments: We thank NASA's Cosmochemistry and Origin of Solar System programs for support. We appreciate a discussion of these issues with Robert Reedy, D. S. Burnett, and P. Vogel. Caltech Contribution #8902 (1104).

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